PROTON MAGNETIC RESONANCE SPECTRA OF POLYCRYSTALLINE α-AND β-NAPHTHOLS

R. C. GUPTA

DEPARTMENT OF PHYSICS, LUCKNOW UNIVERSITY, LUCKNOW, INDIA.

(*Received February* 6, 1968; *Resubmitted June* 24, 1968)

ABSTRACT. Proton resonance spectra have been recorded for poly-crystalline samples of α-and β-Naphthols at temperatures in the range 94°K-323°K.

It has been found that the second moment (mean square width) of the measured spectrum for the temperature at which the lattice is effectively rigid, namely below 94°K is consistent with assumed models of α and β -Naphthols thereby giving an NMR check of molecular structure of these samples. Possibility of phase change suggested by Aihara (1960) hasa also been explained.

INTRODUCTION

Naphthols are fused polynuclear aromatic compounds in which two rings are fused together in the *o*-position as in the case of Naphthalene and Anthracene. They are the Naphthalene derivatives. Crystal structure of α-Naphthol was only partially determined by Kitaigorodski (1949) while that of β-Naphthol has been completely determined by Watson and Hargreave (1958).

The samples of Naphthols were kindly sent by Professor Chojnacki to find whether molecular rotations, if any, in these substances are really the cause of difficulty in obtaining the crystals of these substances from the melt. It was also decided to verify the possible phase change due to the rotation of both types of Naphthol molecules as suggested by Aihara (1959) on the basis of sublimation pressure measurements. Besides checking molecular structure attempts have also been made to verify these suggestions by finding how the second moment and the spin lattice relaxation time of the proton nuclear resonance signal change with temperature between 94°K and 339°K.

EXPERIMENTAL APPARATUS AND METHOD

Proton Magnetic Resonance experiments were performed using a permanent magnet designed by Andrew and Eades, having a field strength of about 6000 gauss. The two inch gap facilitated experiments to be performed at low temperature. Over a volume of 1 cm^3 the field is uniform with in 50 milligauss which is quite sufficient for most solid state work. Investigations at lower temperatures were done utilising liquid air with a view to freeze the molecular motions if any.

---

*Ka-tendra Chemii Fizycznej Wroclaw, Poland.

High temperature measurements were made by using an electrical heater suspended in an oil bath. More details of Proton Magnetic Resonance Spectrometer have been described elsewhere (Gupta 1963).

SECOND MOMENT MEASUREMENTS

The rigid lattice second moment (S_0) was calculated from the theory of Van-Vleck (1948) for polycrystalline sample. The contribution (S_0) consists of two parts intramolecular (S_1) and intermolecular (S_2) contributions. Interamolecular contributions to the second moment arise from the nuclei which reside in the same molecule and calculated from the formula for the protons :

$$S_1 = \frac{6}{5}\left(\frac{I+1}{I}\right)^2 N^{-1}\mu^2 \sum_{j>k} r^{-6}_{jk} \text{ gauss}^2. \quad \ldots \quad (1)$$

where I is the spin number, μ is the magnetic moment, N is the number of magnetic nuclei over which the sum is taken and r_{jk} is the distance between nuclei j and k. In our particular case using Bearden and Watts values (1951), the above equation simplifies to

$$S_1 = \frac{715.9}{N} \sum_{j} \sum_{k} r^{-6}_{jk} \text{ gauss}^2. \quad \ldots \quad (2)$$

The experimental secondmoments were measured from the derivative tracings (figures 1 and 2) and were corrected for the modulation amplitude (Andrew 1953). The following expression was used to evaluate Second moment data.

$$S = \frac{\Sigma h^3 f(h)}{2\Sigma h f(h)} \text{ gauss}^2. \quad \ldots \quad (3)$$

Figure 1

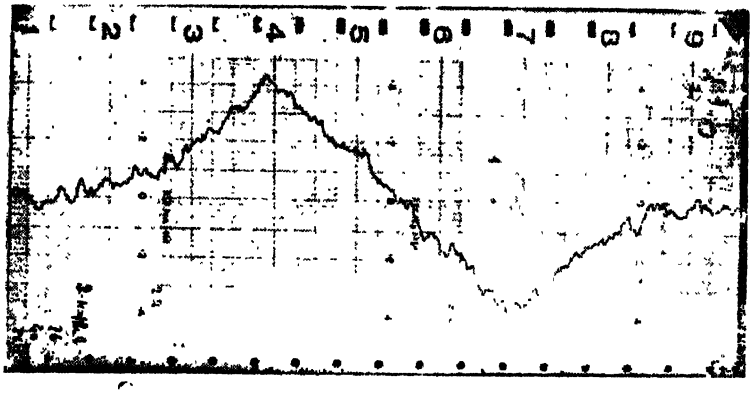
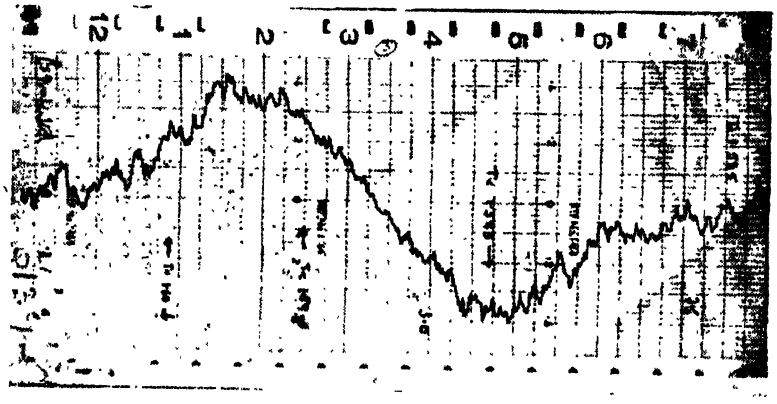


Figure 1



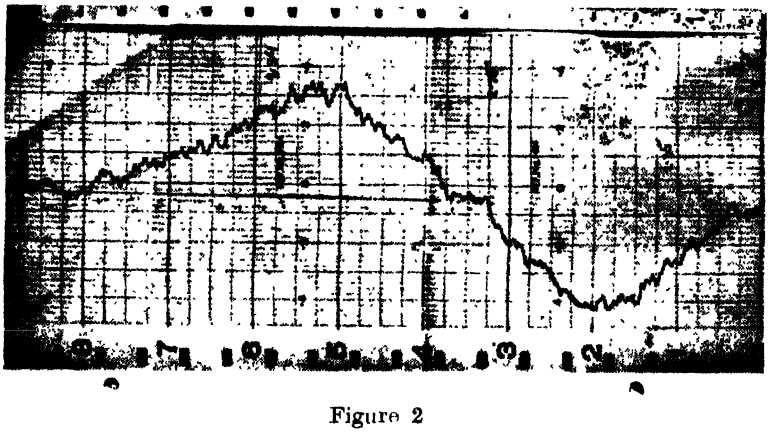


Figure 2

Radio frequency levels used were well below saturation while tracing the lines. All measurements are accurate to ∓ 1 gauss[2] owing to inadequate signal to noise ratio.

SPIN LATTICE RELAXATION-TIME MEASUREMENTS (T_1)

The spin lattice relaxation times were measured by the direct method. Measurement by this method is possible when T_1 is long compared to the time constant of the recording apparatus which in the present case could be varied between 1 sec. and 30 sec.

CRYSTAL STRUCTURE

Crystal structure of α-Naphthol was only partially determined by Kitaigorodski (1949), the inter-atomic distances being unknown. α-Naphthol is monoclinic having four molecules in the unit cell whose dimension are, $a = 13.0$, $b = 4.80$, $c = 13.4$ and $\beta = 117°10'$ and the space group $P2_1/a$.

Crystallographic studies of β-Naphthol (probably of the stable modification) have been mentioned by several workers. Detailed reports by Kitaigorodski (1945 and 1947) include a discussion of the position and the orientation of the molecules and of hydrogen bonding between pairs of molecules. Later, Hargreaves and Watson (1957) found a unit cell and space group different from those deduced by Kitaigorodski. There are eight molecules in the unit cell having dimensions $a = 8.18$Å, $b = 5.95$Å. $c = 36.29$Å and $\beta = 119°52'$ and space group $P2_1/a$, possessing two types of hydrogen bond, each of which links a pair of non equivalent molecules. The $O-O$ distances are 2.72Å and 2.79Å respectively. Every molecule is attached by hydrogen bonds to two neighbours and in this way the molecule is linked into chains. Each chain runs throughout the crystal with its length parallel to the axis a of the monoclinic unit cell. There are no hydrogen-bond linkages between neighbouring chains.

MOLECULAR STRUCTURE

In the absence of any precise data regarding α-Naphthol, we have assumed the same bond distancesand angles as used in the case of β-Naphthol, namely

Carbon to Carbon bond length = 1.38Å
Carbon to Hydrogen bond length = 1.08Å
Carbon to Oxygen bond length = 2.7Å

and usual values of angles of 120° as in the case of benzene molecule.

In β-Maphthol there appears to be some confusion between the values for C–C distances (marked on fig. 6) and various corresponding values of C–C distances as determined by using atomic coordinates found by Watson and Hargreaves (1958). As these values differ quite appreciably, for example the distance 1.38Å marked in the fig. 6 corresponds to a value 1.24Å; hence it is not safe to use atomic coordinates determined by Watson and Hargreaves (1958). Since the Naphthol molecule is essentially two benzene rings fused together, and the above mentioned C–C distance of 1.38Å is quite close to the usual C–C distance found in benzene,

we think it quite reasonable to rely on the marked values rather than those obtained by making use of atomic coordinates given by Watson and Hargreaves.

Further it is assumed that carbon to hydrogen bond length is 1.08Å, carbon to oxygen bond length is 1.36Å and oxygen to oxygen bond length is 2.7Å and angles have the usual value of 120° as found in the case of the benzene molecule.

CALCULATION OF INTRA-MOLECULAR CONTRIBUTION TO THE SECOND MOMENT

Different hydrogen positions

The following table shows the atomic coordinates of the various hydrogen positions found in β-Naphthol molecule, using coordinate system shown in fig. 6.

Table 1

	x	y	z
H_1	−3.38606	1.2500	0
H_2	−3.37720	−1.2500	0
H_3	−1.25570	−2.5150	0
H_4	1.16910	−2.4625	0
H_5	3.29944	1.2450	0
H_6	1.18640	2.4725	0
H_7	−1.25570	2.5150	0
H_8	4.6000	−1.8000	−1.25

The coordinates for the H_8 were found out by making a model and measuring the Z coordinate of H_8.

Using the above proposed model, and equation (2) with $N \mp 8$ the intramolecular contribution to the second moment is calculated to be about 2.6 gauss^2.

As pointed out earlier, there had been some controversy regarding the crystallographic form of β-Naphthol. Besides, as mentioned earlier there appears to be some confusion regarding the atomic coordinates found by Watson and Hargreaves (1958). Consequently we have determined the inter-molecular contribution to the second moment by comparing with some similar substances. As indicated in the case of α-Naphthol we can safely assume inter-molecular contribution to the second moment as 6.5 gauss^2. The calculated second moment for a rigid lattice is therefore 9.1 gauss^2 at 94°K, which appears to be about 1 1 gauss^2 lower than the mean experimental value of 10.1 gauss^2 due to poor signal to noise ratio at this temperature. It is therefore safe to treat lattice to be rigid at 94°K.

Using the above proposed model which is similar to β-Naphthol the intramolecular contribution to the second moment in the case of α-Naphthol is about

2.6 gauss^2. In the absence of any precise information regarding the crystal structure of α-Naphthol, we can find the inter-molecular contribution to the second moment by comparison methods. In the case of the Naphthalene molecule, the intra and inter-molecular contribution to the second moment are 3.2 gauss^2 and 6.9 gauss^2 respectively, thus giving a theoretical second moment of 10.1 gauss^2. Our lower value of the intra-molecular contribution with respect to Naphthalene is probably due to the hydroxy hydrogen; this may also cause an increase in the inter-molecular contribution to the second moment as compared with the Naphthalene molecule and consequently increase the ratio of intra and intermolecular contribution compared with Naphthalene. If we suppose that inter-molecular contribution in α-Naphthol is 6.5 gauss^2, the total theoretical second moment becomes about 9.1 gauss^2 at 94°K for the rigid lattice. The experimental value is about 2 gauss^2 larger than this value and this discrepancy can be attributed as due to inadequate signal to noise ratio obtained at this temperature.

EXPERIMENTAL RESUTS

Second moment and line width variation with temperature

When polycfystalline α-Naphthol was warmed from 94°K to about 333°K, a weak secondary line appeared at about 312°K, which was not clear enough to

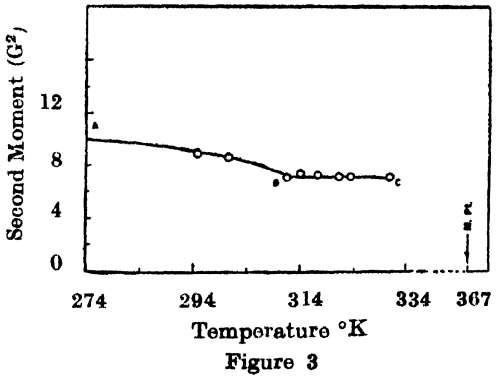


Figure 3

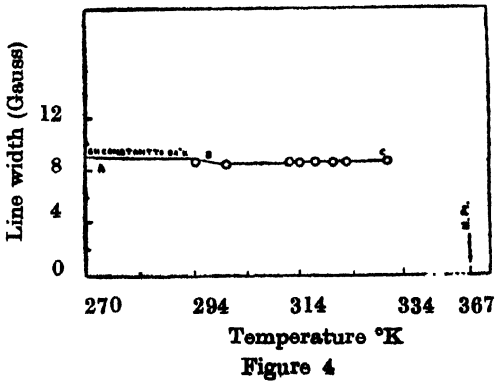


Figure 4

enable any definite conclusions to be drawn. The experimental values of the second moment of about 10.5 gauss^2 (figure 3) and line width of 9.8 gauss (figure 4) were reduced merely to about 8 gauss^2 and 8 gauss respectively.

On warming polycrystalline β-Naphthol from 94°K to about 343°K, there appeared to be some suspicion of some fine structure round about 312°K, which was not marked enough to draw any conclusions. The fall in the observed values of the second moment and the line width was of about the same order as in the case of α-Naphthol (figures 7 and 8 respectively).

Spin lattice relaxation ime (T_1)

The spin lattice relaxation time T_1 in case of α-naphthol was quite large (nearly 29.5 minutes) at 94°K. It was observed to be about 2.3 minutes at room temperature and further decreased to about 1.6 minutes round about 313°K (figure 9).

In case of β-naphthol the spin-lattice relaxation time at 94°K was about 17.5 minutes. It was observed to be about 5.3 minutes at room temperature (288°K) and 2.7 minutes at about 319°K (figure 5).

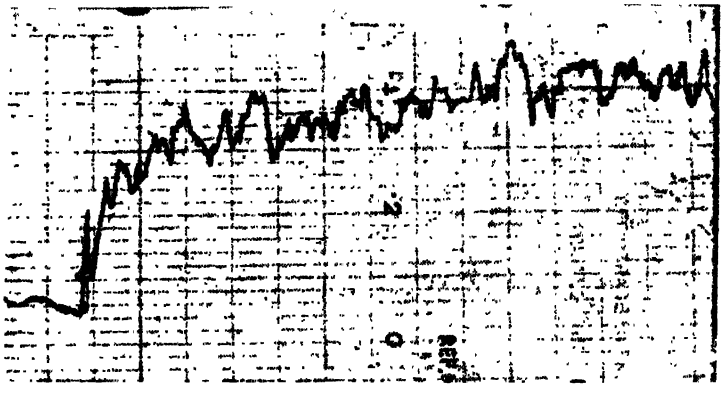


Figure 5

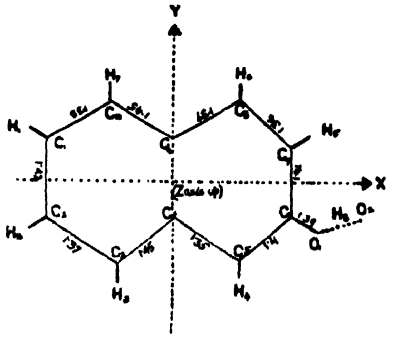


Figure 6

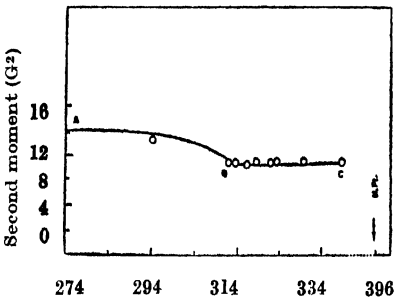


Figure 7

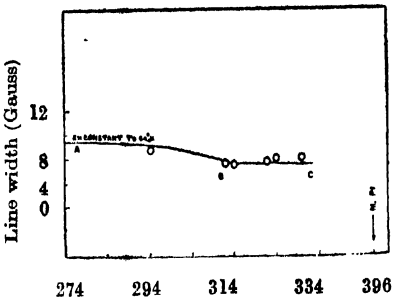


Figure 8

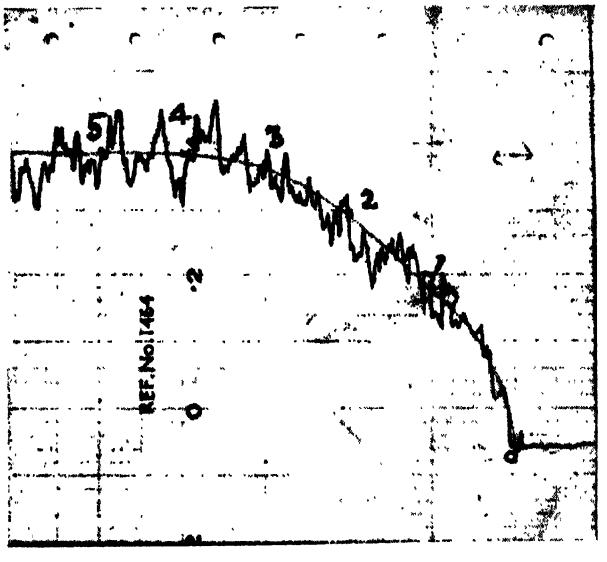


Figure 9

INTERPRETATIONS

The absorption spectrum

The fig. 3 shows the plot of the second moment of the absorption spectrum against temperature in α-naphthol. The portion AB of the curve corresponds to the calculated second moment of the rigid lattice state, where all the effective molecular motion is supposed to have been frozen. The experimental value of about 11 gauss² is in satisfactory agreement with the theoretical value of 9.1 gauss² within the accuracy of the experiment, which gives support to our assumed model.

At about 312°K (point C, figure 3) there was some indication of the appearance of fine structure. This temperature is near enough the temperature at which Aihara (1960) observed a transition in the crystalline state in α-Naphthol (using

sublimation pressure method). We do not agree with the above view, for in our experiment we do not find enough reduction in the value of the second moment or line width. In particular there is no marked discontinuity around 312°K. Furthermore, the α-Naphthol molecule is comparatively large and possesses no symmetry about the C–O bond. Consequently, the rotation of the molecule about this axis does not seen probable and our results suggest that the phase change observed by Aihara is not associated with molecular rotation about C–O bond.

In our experiments, we have observed slight reduction in the values of the second moment from about 312°K, which may be due to vibrational motion of the molecule as observed in the case of the Naphthalene molecule (Andrew, 1950). Probably this sort of motion is associated with wavelength shift due to hydrogen bonding in α-Naphthol (Nagakura and Gouterman, 1957).

The plot of the second moment of the absorption spectrum against temperature in case of β-Naphthol is shown in fig. 8 in which the portion AB of the curve corresponds to the measured second moment of the rigid lattice state, where all the effective molecular motion is supposed to have been frozen. Our experimental value of 10.1 gauss^2 is in satisfactory agreement with the theoretical value of 9.1 gauss^2, supporting our assumed model.

Round about 312°K (point C on the absorption curve), there appeared to be some evidence of a secondary hump. This is nearly the temperature at which Aihara (1960) observed transition in the crystalline states due to possible molecular rotations about C–O bond. In our observations we do not find enough reduction in the observed value of the second moment, and in particular no marked discontinuity was observed around 312°K. Besides the β-Naphthol molecule is comparatively large and possesses no symmetry about the C–O bond. It does not seem probable therefore that rotation would occur about this axis. Our N. M. R. results suggest that the phase change observed by Aihara is not associated with molecular rotation about C–O bond.

The slight reduction in the value of the second moment round about 312°K can be explained in the same way as in the case of α-Naphthol.

ACKNOWLEDGMENT

This work was done in the Nuclear Magnetic Resonance Laboratory at the University College of North Wales, Bangor, U.K. The author is extremely thankful to Prof. E. R. Andrew* and Dr. J. P. LLewellyn for valuable help and discussions.

This work was carried out during the tenure of the Colombo Plan Fellowship, for this the author is very thankful to the British Council.

*Present address : Department of Physics, University of Nottingham, England.

REFERENCES

Aihara, A., 1960, *Bull. Chem. Soc.*, Japan, **33**, 194

Andrew, E. R., 1950, *J. Chem. Phys.*, **18**, 607.

Andrew, E. R., 1953, *Phys. Rev.* **91**, 425.

Bearden, J. A. and Watts, H. M., 1951, *Phys. Rev.* **81**, 73.

Gupta, R. C., 1963, *Ph.D. Thesis*, University College of North Wales, Bangor, U.K.

Hargreaves, A. and Watson, H. C., 1957, *Acta. Crysta.* **10**, 368.

Kitaigorodski, A. I., 1945, *Dokl. Adad. Nauk., S.S.S.R.* **50**, 319.

Kitaigorodski, A. I., 1947, *Izvest. Akad. Nauk, S.S.S.R. Khim. Nauk*, **6**, 561.

Kitaigorodski, A. I., 1949, *I.Z.W. Akad. Nauk., S.S.S.R. Otd. Chim. Nauk*, **8**, 263, 444; 9766d.

Nagakura, S. and Gouterman, M., 1957, *J. Chem. Phys.* **26**, 881.

Van-Vleck, J. H., 1948, *Phys. Rev.* **74**, 1168.

Watson, H. C. and Hargreaves, A., 1958, *Acta Crysta*, **11**, 556.